

IMPROVED QUANTITATIVE ELECTRON MICRO-
PROBE ANALYSIS AT LOW OPERATING
VOLTAGE: II. SULFUR¹

GEORGE A. DESBOROUGH AND ROBERT H. HEIDEL, *U.S.
Geological Survey, Denver, Colorado 80225*

AND

GERALD K. CZAMANSKE,
U.S. Geological Survey, Menlo Park, California 94025

ABSTRACT

The influence of both atomic number and mass absorption coefficient in quantitative microprobe analysis of sulfur in common light-element sulfides is substantially reduced by using an operating voltage of 6 kV. There is no loss in counting precision. A linear relationship of X-ray intensity versus concentration permits use of only a few standards in the analysis of sulfur in copper, iron, nickel and zinc sulfides.

INTRODUCTION

Most electron microprobe laboratories routinely use an operating voltage of 15 kV, or higher, for quantitative analysis of sulfides. Recognizing that the corrections of X-ray intensity data for effects of atomic number (\bar{Z}) and mass absorption coefficients ($\bar{\mu}/\rho$) may increase with increasing operating voltage, we have investigated the suitability of analyzing sulfur at low operating voltages. Synthetic sulfides have been used mainly. The Ni and Fe sulfides were prepared by one of us (G. K. C.); the synthetic sphalerites and one Cu, Fe sulfide were prepared by Paul B. Barton, Jr. The effective atomic number (\bar{Z}), calculated mass absorption coefficient ($\bar{\mu}/\rho$) for $S_{K\alpha}$, and the composition for these samples are given in Table 1 for the 14 samples studied.

ANALYTICAL METHODS

Analyses were performed with an A.R.L. model EMX electron microprobe equipped with ADP crystals on each of three spectrometers, two of the spectrometers (1 and 2, Table 2) have sealed proportional counters, the other (3, Table 2) has a flow counter. Analyses for sulfur were performed on all three spectrometers simultaneously. Fixed beam current count termination gave count times of 10.0 ± 1.0 seconds. An electron beam diameter of about $5 \mu\text{m}$ was used for all analyses. Settings for the three operating conditions of analyses presented in Table 2 were: (1) 15 kV, sample current = 2×10^{-8} A on benitoite, (2) 10 kV, 2×10^{-8} A on benitoite, and (3) 6 kV, 4×10^{-8} A on benitoite.

X-ray intensity data (counts) for each spectrometer were obtained by averaging the counts for 10 observations on each sample. Corrections for background are based on average counts obtained, for each operating condition, at spectrometer settings 0.1865 \AA below and 0.1840 \AA above the $S_{K\alpha}$ peak position respectively. These averaged background corrections ranged from about 40 counts (6 kV) to 55 counts (15 kV). X-ray intensity data presented

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Table 1. The effective atomic number (\bar{Z}), calculated mass absorption coefficient ((μ/ρ)) for $S_{K\alpha}$ and the composition of sulfide samples used for study of effect of operating voltage on X-ray intensity versus sulfur concentration. [Leaders (---) indicate element not present.]

Name and formula	\bar{Z}	(μ/ρ) for $S_{K\alpha}$	Composition (weight percent)					
			S	Fe	Zn	Cu	Ni	As
Pyrite (FeS_2)-----	20.65	666.8	53.45	46.55	---	---	---	---
Orpiment (As_2S_3)-----	26.35	1548.6	39.10	---	---	---	---	60.9
Troilite (FeS)-----	22.35	822.6	36.47	63.53	---	---	---	---
Pyrrhotite ($Fe_{1-x}S$)---	22.10	799.4	39.00	61.00	---	---	---	---
Ni-pyrrhotite-----	22.12	802.4	39.00	60.02	---	---	0.98	---
Ni-pyrrhotite-----	22.24	820.3	38.62	55.59	---	---	5.79	---
Millerite (NiS)-----	23.76	1027.6	35.32	---	---	---	64.68	---
Heazlewoodite (Ni_3S_2)-	24.79	1132.8	26.69	---	---	---	73.31	---
Sphalerite (ZnS)-----	25.39	1285.0	32.91	---	67.09	---	---	---
Sphalerite (Fe,Zn)S---	25.26	1252.4	33.12	4.31	62.47	---	---	---
Sphalerite (Fe,Zn)S---	24.90	1210.3	33.48	10.27	56.25	---	---	---
Sphalerite (Fe,Zn)S---	24.10	1088.6	34.42	26.98	38.60	---	---	---
Chalcopyrite ($CuFeS_2$)-	23.54	997.0	34.94 ₄	30.43 ₂	---	34.62 ₄	---	---
Synthetic ($CuFeS$)-----	25.25	986.0	33.31	37.65	---	34.94	---	---

and discussed here are corrected *only* for background. Instrumental drift was less than 1 percent and is not considered important. Data for each operating condition were acquired in less than 1½ hours.

X-RAY INTENSITY VERSUS SULFUR CONCENTRATION

Figure 1 presents data for one spectrometer showing net counts versus sulfur concentration for 14 sulfide samples analyzed at 15 kV, 10 kV,

Table 2. Mean sensitivity (\bar{S}), standard deviation for 10 observations in counts per weight percent sulfur (σ), coefficient of variation (CV), for sulfur at 15, 10, and 6 kV in the 12 synthetic and 2 natural sulfides.

15 kV			10 kV			6 kV		
\bar{S}	σ	CV	\bar{S}	σ	CV	\bar{S}	σ	CV
Spectrometer 1								
857.5	39.8	4.6	510.7	10.7	2.1	386.8	3.9	1.0
Spectrometer 2								
919.3	46.4	5.1	539.3	13.7	2.5	393.6	4.8	1.2
Spectrometer 3								
272.1	15.4	5.7	150.8	4.4	2.9	Insufficient intensity		

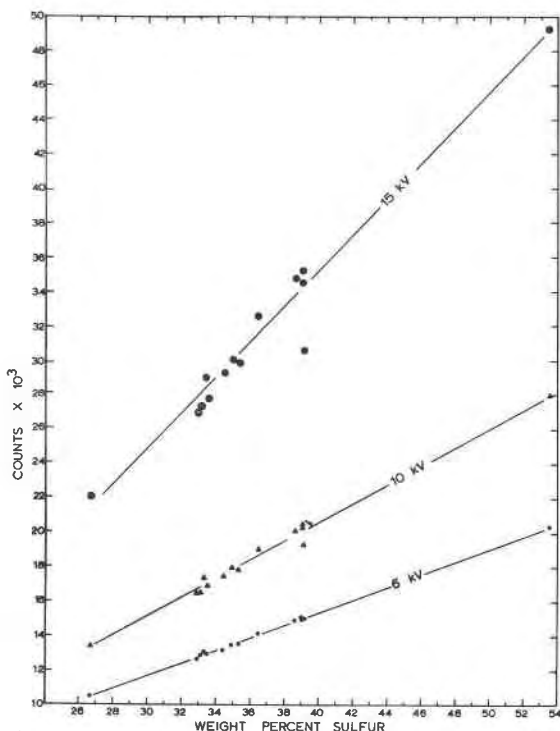


FIG. 1. Concentration of sulfur versus net X-ray intensity (counts) for 14 sulfide samples analyzed at 15, 10, and 6 kV on one spectrometer. Size of data points is proportional to standard deviation (σ) of counts.

and 6 kV. Data point size reflects uncertainties due to both counting precision and sample inhomogeneity. It is evident that at 6 kV, X-ray intensity (counts) is directly proportional to sulfur concentration for the concentration range studied. At 15 kV, however, there is considerable scatter.

Standard deviations (σ) for 10 observations on FeS (troilite, 39.00 weight percent sulfur) and FeS₂ (pyrite, 53.45 weight percent sulfur) are given in Table 3 for evaluation of both sample homogeneity and analytical uncertainty at each operating voltage. On the basis of these σ values for troilite and pyrite, analytical error at 15 kV is no greater than at 6 kV.

Through use of the relationship $S = \text{counts per weight percent concentration}$, the magnitude of the effects of atomic number and mass absorption on X-ray intensity at different voltages may be evaluated, the constancy of S for sulfur in a series of samples being a measure of the linearity of the relationship between concentration and X-ray intensity.

Table 3. Standard deviation (σ) in weight percent sulfur for 10 observations on FeS (troilite, 39.00 weight percent sulfur) and FeS₂ (pyrite, 53.45 weight percent sulfur) at 15, 10, and 6 kV on each of three spectrometers.

wt. % S	15 kV	10 kV	6 kV
	σ	σ	σ
Spectrometer 1			
39.00	0.34	0.28	0.39
53.45	0.22	0.15	0.18
Spectrometer 2			
39.00	0.34	0.33	0.32
53.45	0.39	0.17	0.37
Spectrometer 3			
39.00	0.30	0.48	(Insufficient
53.45	0.43	1.18	intensity)

We have determined values of S for each of our observations. By averaging all 14 values of S for each spectrometer at each operating voltage, we obtain \bar{S} , σ (standard deviation), and CV (coefficient of variation = $(\sigma/\bar{S}) \times 100$) which are presented in Table 2. Counts for the flow counter (spectrometer 3) at 6 kV are too low to be meaningfully included in Table 2.

Deviations from linearity of X-ray intensity versus sulfur concentration data illustrated on Figure 1 may be evaluated in terms of coefficient of variation (CV , Table 2). Systematic decrease in CV from 15 to 6 kV (Table 2) is attributed to the greater influence of both mass absorption coefficient and effective atomic number at higher operating voltages. Demonstrations of each of these effects is illustrated on Figure 2A and B.

Counts per weight percent sulfur- (S) versus effective atomic number (\bar{Z}) (Figure 2A), and (S) versus mass absorption coefficient for $S_{K\alpha}$ (Figure 2B) are shown for each sample for each operating voltage. The relationship of counts per weight percent sulfur, versus effective atomic number and mass absorption coefficient for $S_{K\alpha}$, respectively, at 15 kV, compared to 10 and 6 kV, indicates to us that the influence of these corrections (effective atomic number and mass absorption coefficient) on $S_{K\alpha}$ X-ray intensity for the sulfides studied is significantly reduced by using an operating voltage of 6 kV.

The effects of \bar{Z}/A on X-ray intensity, which incorporates both atomic number (\bar{Z}) and atomic weight (A) functions, have been graphed in terms of counts per weight percent sulfur for all samples studied. No

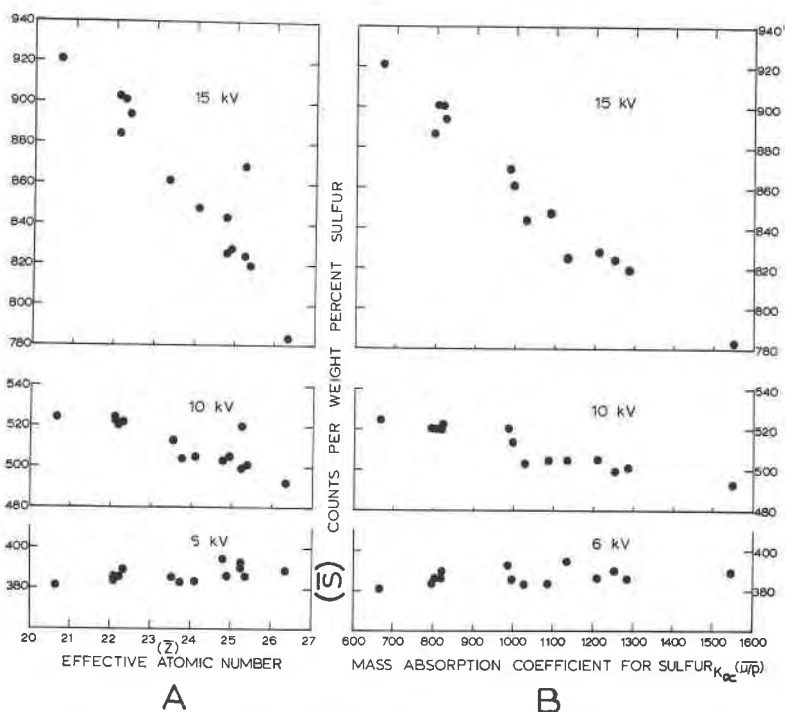


FIG. 2. A, Effective atomic number (\bar{Z}), and B, mass absorption coefficient ($\bar{\mu}/\rho$) for $S_{K\alpha}$ versus counts per weight percent sulfur (\bar{S}) for 14 samples analyzed at 15, 10, and 6 kV on one spectrometer.

systematic relationship was observed and \bar{Z}/A relations are not illustrated.

CONCLUSIONS

The relationship of X-ray intensity (counts) to sulfur concentration in the common, light-element sulfides is essentially linear, within the limitations of counting precision and sample homogeneity, at an operating voltage of 6 kV. Deviations from linearity at 15 kV are chiefly due to effects of both effective atomic number (\bar{Z}) and mass absorption coefficient ($\bar{\mu}/\rho$).

Numerous standards may be eliminated in the determination of sulfur concentration if an operating voltage of 6 kV is used. Also, a linear calibration curve relating X-ray intensity to sulfur concentration eliminates the need for using complex computer corrections required at higher operating voltages.

We note that counting precision for sulfur is no better than about

0.3 percent of the amount present at one standard deviation, under ideal conditions of sample homogeneity in the concentration range of about 25–50 weight percent sulfur; *i.e.*, 50.00 ± 0.30 weight percent at the 95 percent confidence level (2σ) is a more realistic reported value. In view of this opinion, reported sulfur values such as 42.63 weight percent are not realistic. Also we suggest that some value in terms of analytical variations (*e.g.*, standard deviation, coefficient of variation, etc.) should be reported; these may be determined with minimal effort and are of substantial value in assessment of data.

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